

Supplementary content

Fabrication of hierarchical multilayer poly(glycerol sebacate urethane) scaffolds based on ice-templating

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Macroscopic images of the custom-made moulds

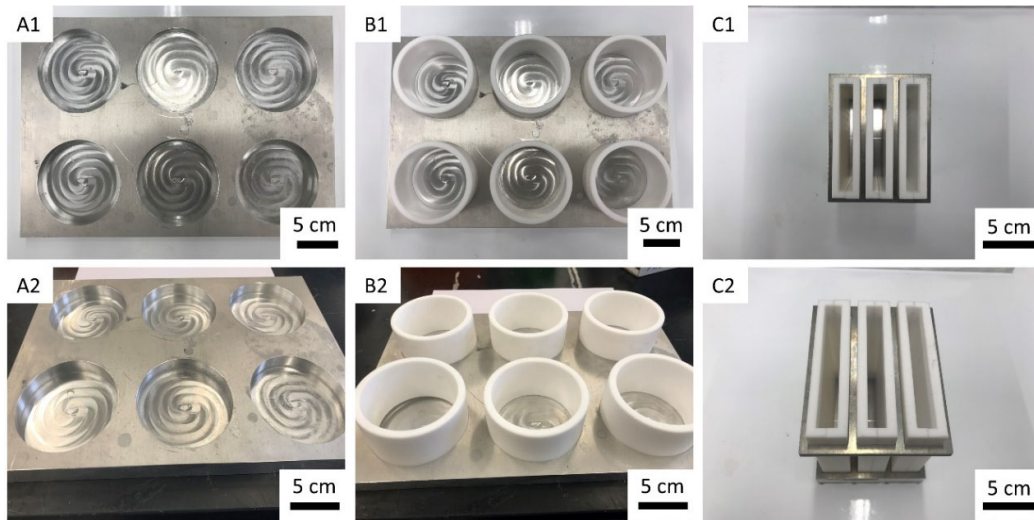


Figure S1: Inhouse designed moulds with aluminium base and PTFE walls for multiple orientation scaffold fabrication. (A1) Top view of mould-isotropic (aluminium all-around, diameter: 100 mm), (A2) side view of mould-isotropic, (B1) Top view of the mould-perpendicular (diameter: 85 mm), (B2) side view of mould-perpendicular, (C1) top view of mould-parallel (width x depth: 10 x 100 mm) and (C2) side view of mould-parallel.

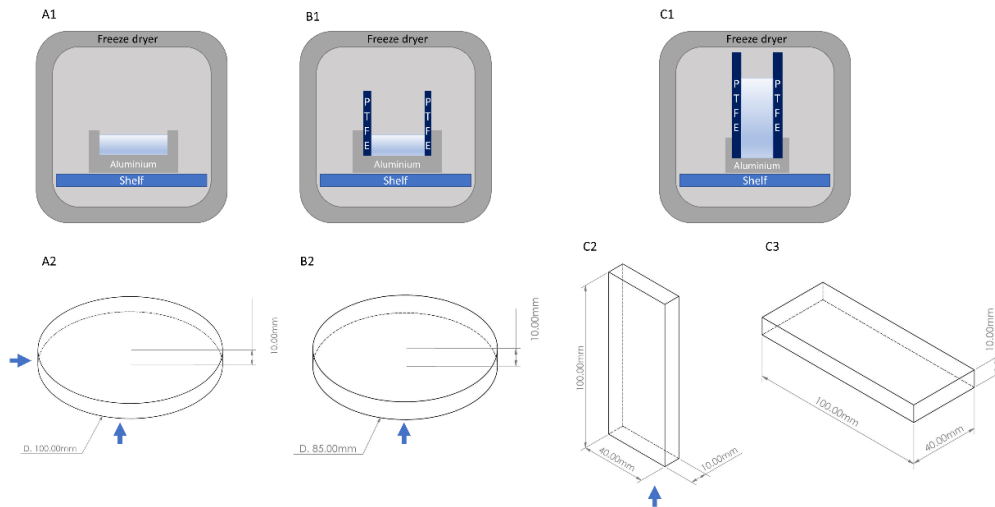


Figure S2: Schematic showing the custom-made moulds in the freeze dryer and the scaffold dimensions. (A1) Mould-isotropic, (A2) PGSU-bilayer/PGSU-trilayer, (B1) mould-perpendicular, (B2) PGSU-perpendicular, (C1)

mould-parallel, (C2) PGSU-parallel as produced and (C3) PGSU-parallel as used. The blue arrows show the sides of the scaffold that were in contact with the aluminium base. Schematics are not scaled.

Mould characterisation – polymer solution freezing rate

The temperature gradient of the PGSU pre-polymer solution (10 % w/v) during the pre-freeze stage was recorded using a temperature probe at three different locations for all three moulds. For the mould-isotropic and mould-perpendicular, a temperature probe was placed inside the PGSU pre-polymer solution at positions 0 mm (top), 5 mm (middle) and 10 mm (bottom) as soon as the pre-freeze stage began, and the temperature was recorded every minute for a total of 3 h. For the mould-parallel a temperature probe was placed at 0 mm (bottom), 20 mm (middle) and 40 mm (top). Following the method described in [1], the nucleation event was defined as the

temperature point where the solution reached the melting point (T_m) of 1,4-dioxane (11.7 °C).

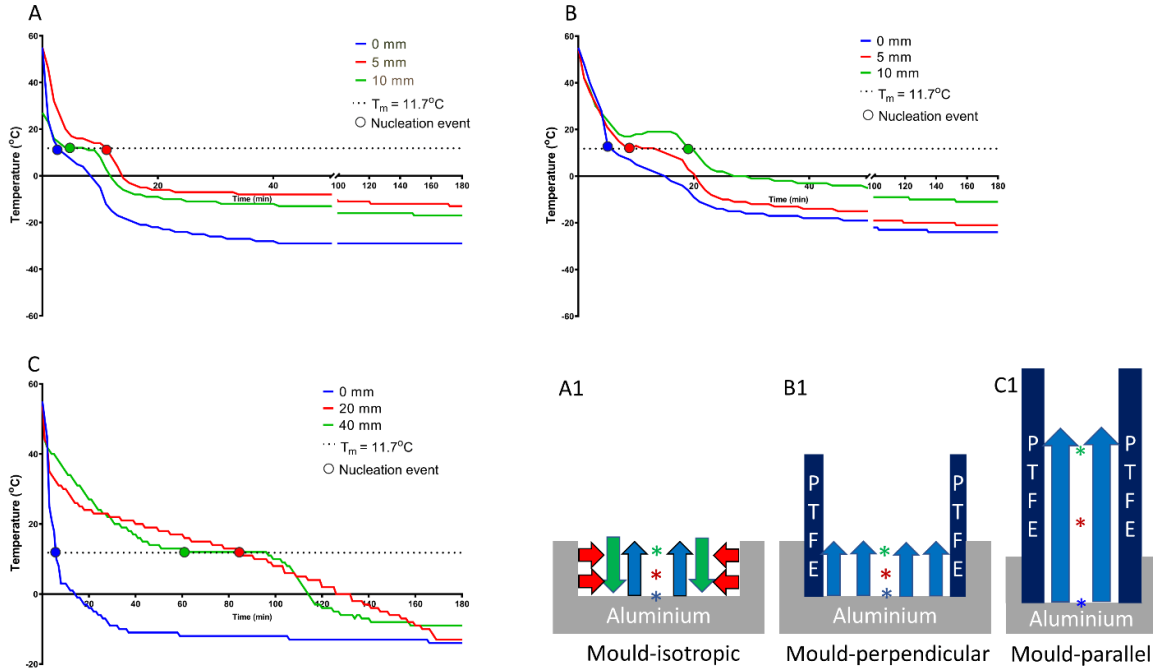


Figure S3: Thermal profile of the PGSU pre-polymer/1,4-dioxane solution during freezing using the (A) mould-isotropic, (B) mould-perpendicular and (C) mould-parallel. T_m = melting point of 1,4-dioxane. The schematics represent the (A1) mould-isotropic, (B1) mould-perpendicular and (C1) mould-parallel and the freezing direction (blue and green arrows) of the pre-polymer solution (schematics are not scaled).

The thermal profile of the in-house build moulds was characterised to understand how each mould and its design can affect the freezing behaviour of the PGSU pre-polymer solution therefore the pore architecture of the PGSU scaffolds.

In view of mould-isotropic, the nucleation event of the PGSU solution happened first at the 0 mm then 10 mm and finally at 5 mm (see Figure S3 - A and A1), indicating that the solution froze from the two outer surfaces to the inside. The other

two nucleation events occurred at 3 min for the 0 mm and 5 min for the 10 mm and 11 min for the 5mm.

Regarding the mould-perpendicular, the nucleation event happened first at the 0 mm point at 6 min, and then at the 5 mm position at 14 min and last at the 10 mm at 20 min (see Figure S3 – B and B1). This means that the PGSU pre-polymer solution froze from the bottom to the top, as expected. Additionally, the whole solution froze within the first 20 min, with only 14 min separating the first nucleation event to the last.

The thermal profile of mould-parallel is shown in Figure S3 – C and C1. The bottom of the solution, at 0 mm, had its nucleation point 6 min after the start of the experiment followed by the mid part of the solution at 20 mm after 85 min. Finally, the whole solution froze at 97 min. Therefore, the whole solution froze very slowly, and the nucleation events had 91 min difference between the bottom and the top of the solution.

References

1. Pawelec, K.M., et al., *A design protocol for tailoring ice-templated scaffold structure*. J R Soc Interface, 2014. **11**(92): p. 20130958.